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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

GUY LUMIA, ET AL.

: EXAMINER: CARRILO, BIBI S.

SERIAL NO: 10/089,162 :

FILED: MARCH 27, 2002

: GROUP ART UNIT: 1746

FOR: PROCESS FOR TREATMENT AND :  
EXTRACTION OF ORGANIC CORK  
COMPOUNDS BY A DENSE FLUID  
UNDER PRESSURE

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes Jean-Marie ARACIL who deposes and states that:

1. I am a named inventor in the above-identified application.
2. I am a graduate of Chemistry and received my Ph degree in the year 1991.
3. I have been employed by SABATE (now OENEO BOUCHAGE) since 1992, and I have been conducting research in the field of extraction of 2,4,6-TCA by supercritical CO<sub>2</sub> for 8 years.
4. I have reviewed and understood the contents of Chouchi ("SFE of Trichloroanisole from Cork," The 40<sup>th</sup> International Symposium on Supercritical Fluids, May 11-14, 1997 Japan) and Maricato ("Etude De l'Extraction Du Trichloroanisole Par CO<sub>2</sub> Supercritique," 1995) cited by the Examiner against the claims of the above-identified application.

5. In order to compare the closest prior art cited by the Examiner with the claimed invention, the following experiments were carried out by me or under my direct supervision and control.

6. A first set of tests was conducted under static conditions (e.g., Chouchi uses a static operating condition : see scheme 1). Extraction of a native TCA-contaminated cork material having a releasable amount of 2,4,6-TCA of 7.1 ng/l was subjected to extraction with a dense fluid under pressure.<sup>1</sup> The extraction was carried out at 40°C at a pressure was 140 bars achieved after a duration in pressurize of 20 minutes, the contact time described in the tables below, and for a duration of return to atmospheric pressure of 90 minutes. The dense fluid under pressure was supercritical CO<sub>2</sub>. Table 1 describes the releasable amount of TCA remaining in the cork after extraction while Table 2 shows the extraction efficiency.

Scheme 1

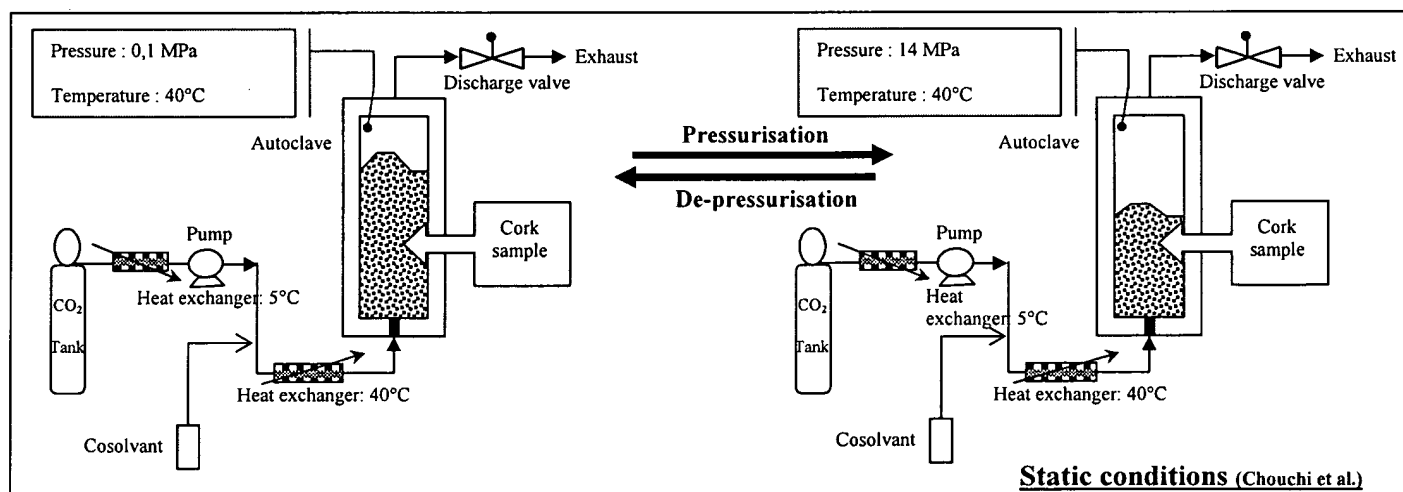


Table 1

Initial cork moisture	Contact time	Solvent rate	Amount of releasable TCA Remaining After Extraction (ng/l)	
			"Dry" CO <sub>2</sub>	CO <sub>2</sub> + cosolvent (0.2% water (w/w))
3%	10 min	30 kg/kg	4.0	3.7
15%	10 min	30 kg/kg	4.1	3.5
3%	60 min	30 kg/kg	4.2	3.7
15%	60 min	30 kg/kg	4.3	3.4

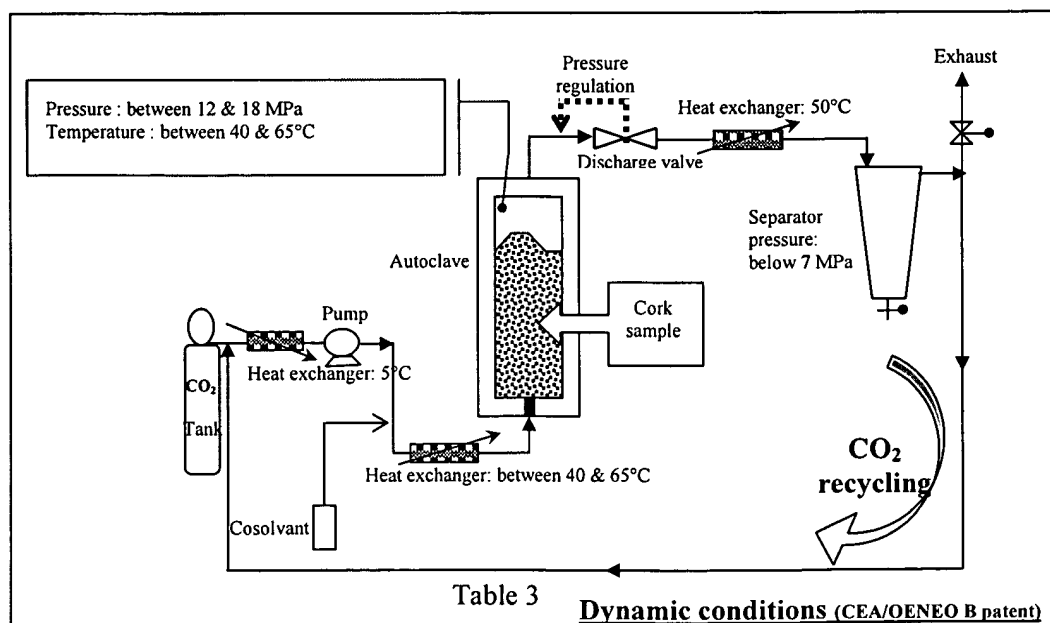
<sup>1</sup> TCA = 2,4,6-Trichloroanisole

Table 2

Initial cork moisture	Contact time	Solvent rate	Extraction Efficiency (%). <sup>2</sup>	
			"Dry" CO <sub>2</sub>	CO <sub>2</sub> + cosolvent (0.2% water (w/w))
3%	10 min	30 kg/kg	44%	48%
15%	10 min	30 kg/kg	42%	51%
3%	60 min	30 kg/kg	41%	48%
15%	60 min	30 kg/kg	39%	52%

7. A second set of extraction tests was conducted using the same native contaminated cork as for the first set of tests. The conditions for the second set of tests were the same as the conditions for the first set of tests except that the extraction was carried out dynamically (see scheme 2 (e.g., the fluid, supercritical state, is depressed by valve discharge to reach gaseous state in separator to demix fluid from contamination. The gaseous fluid (cleaned by state changing) is recycling via the pump to the autoclave again. We renew several times the fluid in the contact of the cork in the extraction cycles up to reach the right quantity of solvent :the solvent rate). The results of the second set of tests are shown below in Tables 3 and 4.

Scheme 2



<sup>2</sup> Extraction Efficiency =  $[1 - (\text{Amount of releasable TCA remaining after Extraction} / \text{Initial Amount of releasable TCA})] \times 100$

Initial cork moisture	Residence time	Solvent rate	Amount of TCA Remaining After Extraction (ng/l)			
			"Dry" CO <sub>2</sub>	CO <sub>2</sub> + cosolvent (0.2% water (w/w))	CO <sub>2</sub> + cosolvent (2% Ethanol (w/w))	CO <sub>2</sub> + cosolvent (2% Butanol/Iso propanol (w/w))
3%	13 min	30 kg/kg	1.5	QL	2.0	1.9
15%	13 min	30 kg/kg	1.7	0.7	1.9	2.5
3%	13 min	100 kg/kg	1.4	QL		
15%	13 min	100 kg/kg		< QL		
3%	13 min	500 kg/kg		< DL		0.5

QL Quantification limit 0.5 ng/l

DL Detection limit 0.2 ng/l

Table 4

Initial cork moisture	Residence time	Solvent rate	Extraction Efficiency (%)			
			"Dry" CO <sub>2</sub>	CO <sub>2</sub> + cosolvent (0.2% water (w/w))	CO <sub>2</sub> + cosolvent (2% Ethanol (w/w))	CO <sub>2</sub> + cosolvent (2% Butanol/Iso propanol (w/w))
3%	13 min	30 kg/kg	79%	93%	72%	73%
15%	13 min	30 kg/kg	76%	90%	73%	65%
3%	13 min	100 kg/kg	80%	93%		
15%	13 min	100 kg/kg	76%	94%		
3%	13 min	500 kg/kg		> 99%		93%

8. Tables 1 and 2 above show that under static extraction conditions a greater amount of TCA is removed when cork is contacted with a dense fluid under pressure when the dense fluid comprises a co-solvent (e.g., water). The efficiency of extraction is seen in Table 2. Carrying out the extraction with "dry CO<sub>2</sub>" (i.e., CO<sub>2</sub> to which no co-solvent has been added) provides an extraction efficiency that is 4% or more lower than the extraction efficiency obtained when the static extraction is carried out with a dense fluid under pressure comprising a co-solvent. The addition of the cosolvent provides a difference in extraction efficiency that ranges from a 4% improvement to a 13% absolute improvement in extraction efficiency.

The results (amount of TCA after extraction) given in tables 1 & 3 don't show any differences between cork with 3% or 15% of moisture. Water of cork is not available to

participate at the extraction process. It would be possible that moisture and/or water can't be use as an efficient cosolvent.

The tests carried out under dynamic conditions show an even greater reduction in TCA can be obtained when alternately increasing and decreasing the pressure while contacting the dense fluid with the cork. For example, the best TCA extraction efficiency obtained with "dry" CO<sub>2</sub> under dynamic conditions is 80% (see Table 4 above). In contrast, a dynamic extraction carried out with a dense fluid under pressure that contains a co-solvent (e.g., water) provides an extraction efficiency of at least 90% and as high as 99%.

9. It is my opinion that the data shown above proves that extracting or cork or a cork-based material with a dense fluid under pressure that contains a co-solvent provides a significantly improved extraction of undesirable compounds such as TCA. It is further my opinion that one of ordinary skill in the art would not foresee such an improvement because undesirable compounds such as TCA have low water solubility therefore one may not expect improved removal of compounds such as TCA when a co-solvent (e.g., water) is added to the solvent (e.g., dense fluid under pressure-CO<sub>2</sub>) before carrying out the extraction.

10. The efficiencies for both the static and dynamic tests tabulated above represent statistically and commercially important improvements because the reduction of a small amount of a undesirable compound such as TCA may lower the amount of the undesirable compound below the threshold detection limit of an individual exposed to a food stuff contaminated with the TCA (e.g., a wine drinker).

11. The results above are statistically significant. By chromatographic analysis the quantification limit for the TCA test is 0.5 ng/l and the detection limit is 0.2 ng/l.

12. The results above are commercially significant because the human sense of taste and smell can detect amounts of TCA at very low levels and the extraction efficiencies

obtained with the claimed process lowers the amount of TCA in the cork to a level that would make its presence on wine lower than the threshold detection level of most humans.

13. The claimed process is commercially successful as shown by the fact that it is carried out on a industrial scale as evidence by the attached photographs of a facility in San Vicente de Alcantara that uses the claimed process.

14. The improvement in the ability to remove greater amounts of TCA when a cosolvent has been added to the dense fluid (dynamic process) is observed on a industrial scale (3000 tons/year) in the San Vicente de Alcantara plant. In Table 5 below, the process was tested at start-up. Samples 1 and 2 were run with only the dense fluid under pressure. The amount of TCA was reduced from an initial concentration of 16 ng/l to 0.8 ng/l. When the process was carried out after adding a cosolvent to the dense fluid, the TCA was reduced below the detection limit of the analytical technique.

Table 5

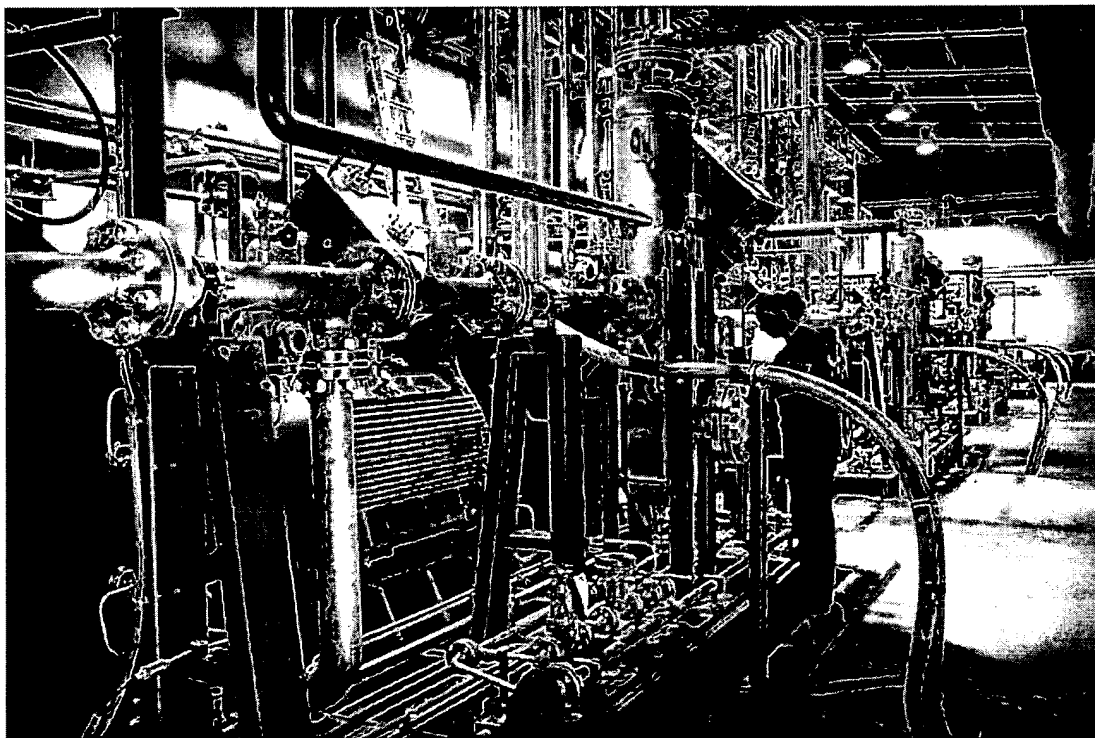
Batch (550 kg) No.	Initial TCA Content (ng/l)	Dense Fluid	Cosolvent	TCA after Extraction (ng/l)
1	16	CO <sub>2</sub>	none	0.8
2	16	CO <sub>2</sub>	none	0.6
3	12	CO <sub>2</sub>	Water	N.D.
4	15	CO <sub>2</sub>	Water	N.D.
5	17	CO <sub>2</sub>	Water	N.D.
6	17	CO <sub>2</sub>	Water	N.D.
7	15	CO <sub>2</sub>	Water	N.D.

N.D. = not detected.

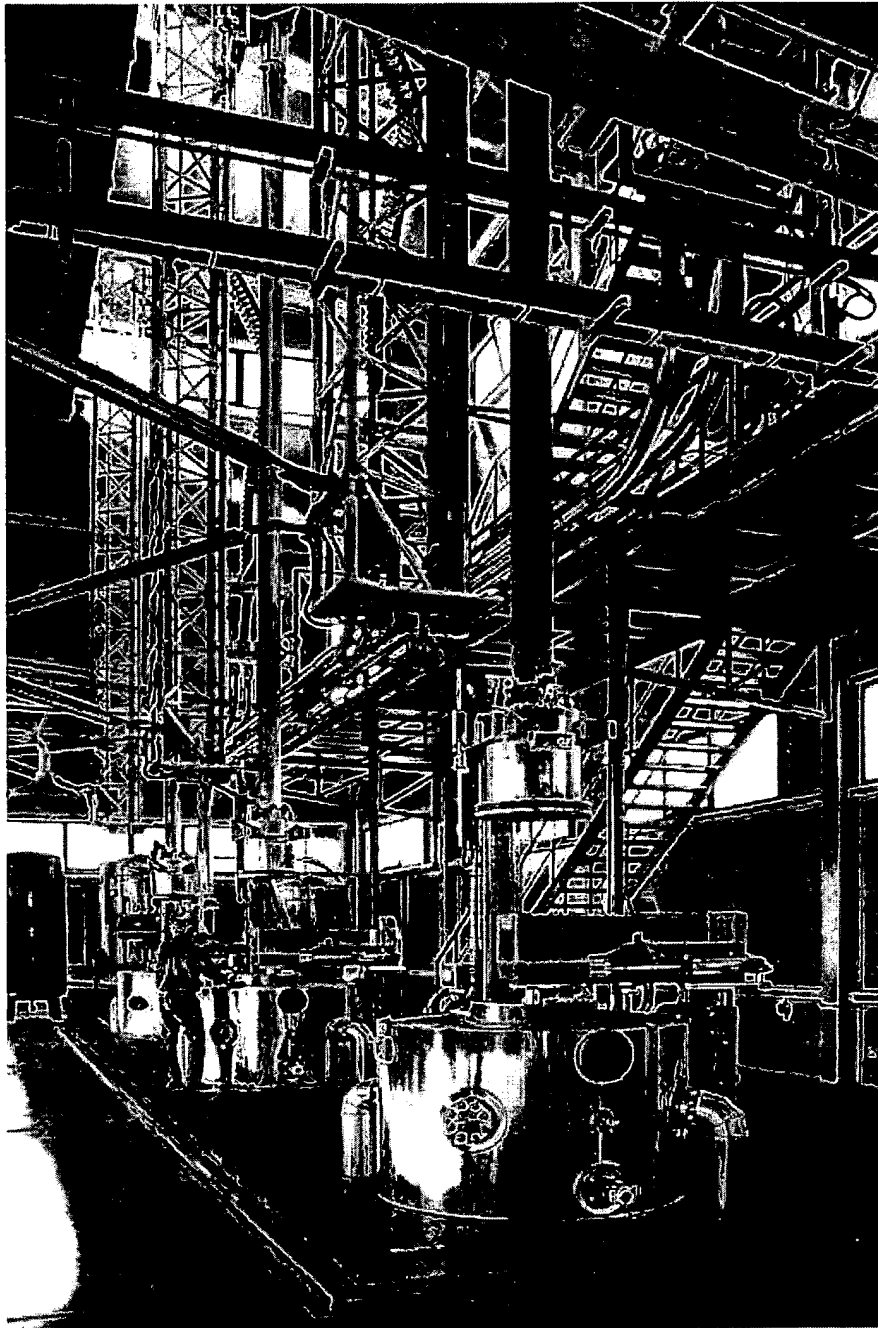
DL Detection limit 0.2 ng/l

15. I have reviewed and understand the scope of the claims in the above-identified application. The improvements in TCA extraction and the improvements in extraction efficiency would, in my opinion, be observed for processes carried out with CO<sub>2</sub> as the solvent and water as the co-solvent over the entire temperature, pressure and compositional requirements recited in the present claims.

VIEW OF COMPRESSORS

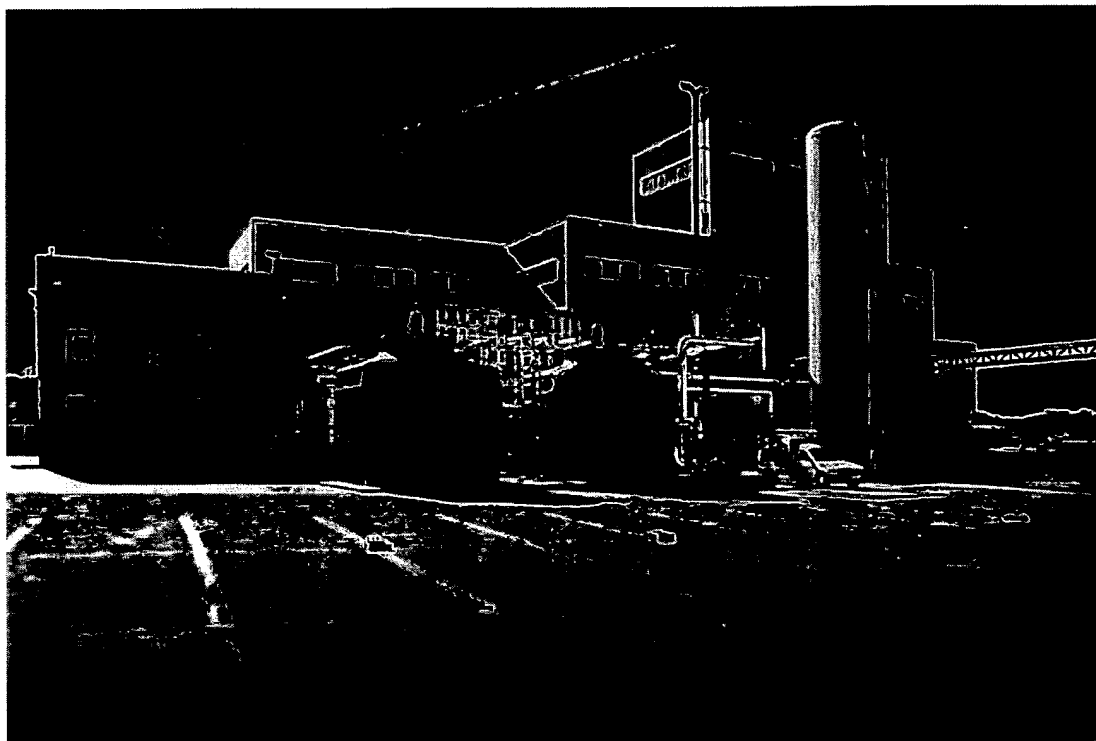


VIEW OF AUTOCLAVES



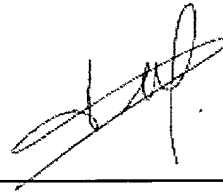


VIEW OF PLANT



16. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true. Further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

17. Further Declarant saith not.

A handwritten signature in black ink, consisting of a series of loops and a long horizontal stroke, positioned above a solid horizontal line.

Signature

November 28th, 2005

Date